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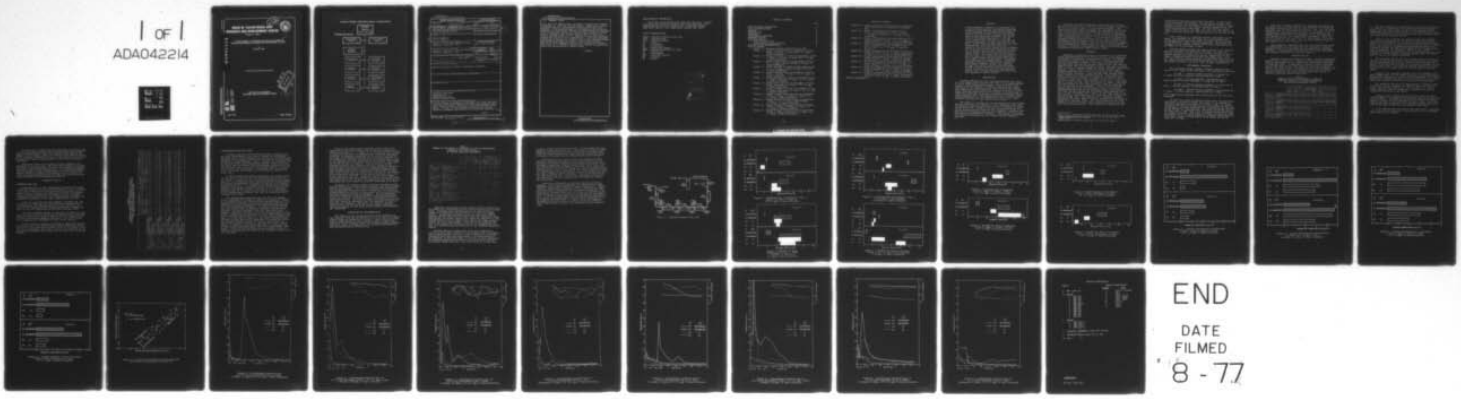

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Report 77-0072

DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20084

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EFFECTIVENESS OF FERROUS SULFATE AS AN INHIBITOR FOR SULFIDE-INDUCED CORROSION OF COPPER-NICKEL ALLOYS

by
Harvey P. Hack

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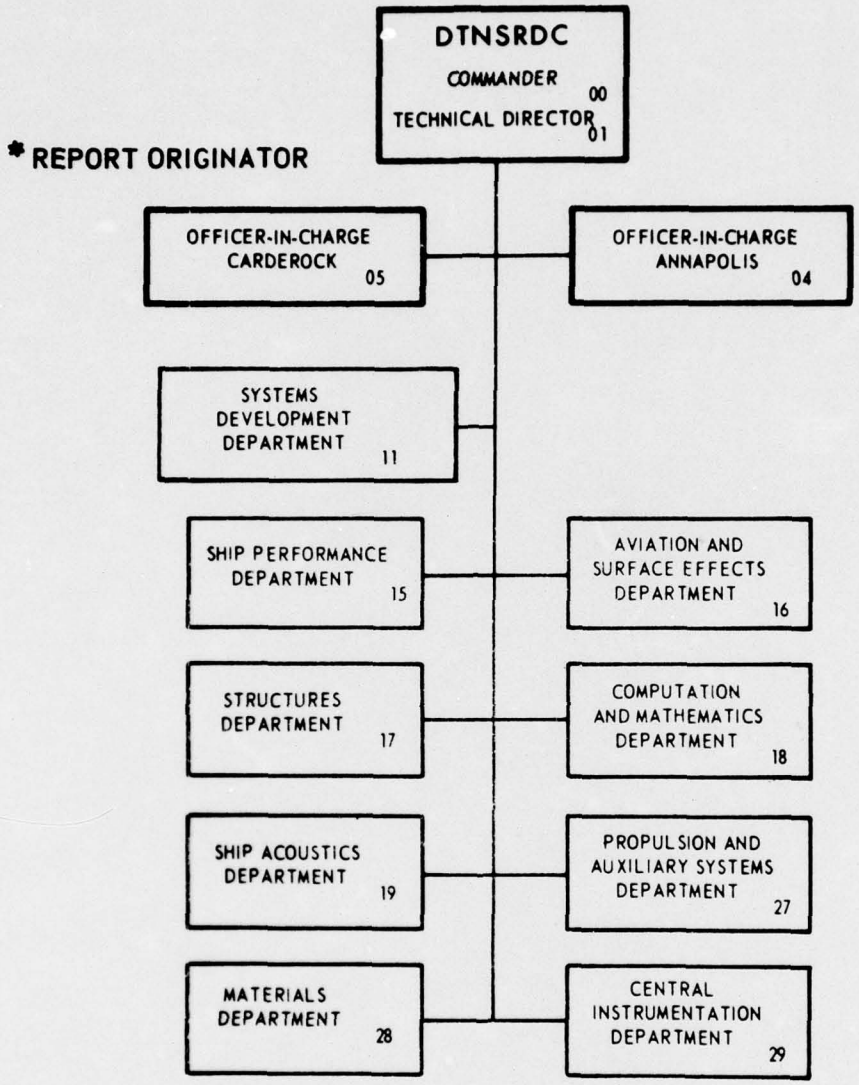

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A large program is ongoing to investigate the causes and solutions for accelerated corrosion of ships piping systems experienced during and after outfitting in polluted brackish harbor waters. As part of this program, various ferrous sulfate inhibitor treatments were evaluated in laboratory exposures of

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20. ABSTRACT (Cont)

90-10 and 70-30 copper-nickel specimens to seawater and seawater containing 0.2 parts per million sulfide. Weight loss, maximum thickness loss, and instantaneous corrosion rate data were obtained. Neither pretreatment by the inhibitor before sulfide exposure nor intermittent inhibitor treatment during sulfide exposure significantly reduced the sulfide-induced attack on either alloy. Treatment after sulfide exposure did not reduce the sulfide-induced attack on 90-10 copper-nickel and only partially reduced the attack on 70-30 copper-nickel. Continuous treatment completely eliminated the attack on both alloys, probably because the inhibitor stripped the harmful sulfides from solution. Results of these exposures should not be generalized to predict the action of the inhibitor against lower sulfide concentrations which have been measured in harbor waters.

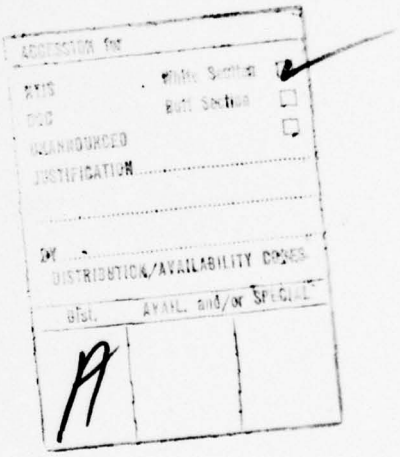
(Author)

ADMINISTRATIVE INFORMATION

This work was performed under Work Unit 2813-606, covering prevention and control of copper-nickel pipe corrosion. The project managers for this work are Mr. E. Marchal, NAVSEA (PMS 393E), and Dr. H.H. Vanderveldt, NAVSEA (SEA 03522).

LIST OF ABBREVIATIONS

ASWTL - Alternate Seawater Test Loop
conc - concentration
ft/s - feet per second
hr - hours
kg - kilograms
mm - millimetres
m/s - metres per second
MSWTL - Modified Seawater Test Loop
mV - millivolts
μm - micrometres
ppm - parts per million
SW - seawater
yr - years



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ABSTRACT

A large program is ongoing to investigate the causes and solutions for accelerated corrosion of ships piping systems experienced during and after outfitting in polluted brackish harbor waters. As part of this program, various ferrous sulfate inhibitor treatments were evaluated in laboratory exposures of 90-10 and 70-30 copper-nickel specimens to seawater and seawater containing 0.2 parts per million sulfide. Weight loss, maximum thickness loss, and instantaneous corrosion rate data were obtained. Neither pretreatment by the inhibitor before sulfide exposure nor intermittent inhibitor treatment during sulfide exposure significantly reduced the sulfide-induced attack on either alloy. Treatment after sulfide exposure did not reduce the sulfide-induced attack on 90-10 copper-nickel and only partially reduced the attack on 70-30 copper-nickel. Continuous treatment completely eliminated the attack on both alloys, probably because the inhibitor stripped the harmful sulfides from solution. Results of these exposures should not be generalized to predict the action of the inhibitor against lower sulfide concentrations which have been measured in harbor waters.

INTRODUCTION

Serious corrosion of 90-10 and comparatively mild attack on 70-30 copper-nickel has been observed in the piping systems of naval ships during construction. These ships have been exposed to an environment of brackish coastal harbor water. The cause of the corrosion, which takes the form of discrete, sharp-edged pits and is generally confined to areas of turbulence, has been attributed to the presence of sulfide ions in sufficient quantities to modify the normally protective copper-oxide corrosion film. This modification of the surface film, through mechanical and electrochemical means, causes rapid localized corrosion of the copper-nickel alloys.

The Center is carrying out an investigation of the sulfide-induced corrosion, with emphasis on the conditions under which the different piping alloys incur attack, and methods of eliminating the attack. Among the methods being explored are the use of ferrous sulfate inhibitor and stripping of sulfides from solution by electrolytically generated chlorine, ferrous ions, and direct electrochemical reduction. This report of investigation concerns evaluation of the ferrous sulfate inhibitor approach.

Experience on some copper-base alloys used in land-based power plants, which have a similar corrosion problem, has led to the use of ferrous sulfate as a corrosion inhibitor. This inhibitor has been shown to promote the development of an iron-rich surface film[1] which may render the substrate alloy resistant to sulfide-induced attack. Ferrous sulfate is generally added intermittently once or twice per day in this application, with highly beneficial results. It is therefore of interest to determine whether ferrous sulfate will be just as effective in eliminating sulfide-induced attack on the copper-nickel alloys in shipboard piping systems. The objective of these experiments was to determine the effectiveness of several ferrous sulfate inhibitor treatments in preventing or countering sulfide-induced accelerated corrosion of copper-nickel alloys.

APPARATUS

Exposures in modified seawater environments were performed in the Modified Seawater Test Loop at the F.L. LaQue Corrosion Laboratory at Wrightsville Beach, North Carolina. The MSWTL,* illustrated schematically in figure 1, is a nonrecirculating seawater loop made of nominal 2-inch polyvinyl chloride pipe with removable sections for housing sample holders and taps for sampling water near each removable section. The loop is fitted, with a series of injection pumps for adding controlled amounts of reagents, such as sodium sulfide or ferrous sulfate, and a chlorine generator unit at the exit to oxidize any remaining sulfide before discharge. Each removable pipe section houses three cylindrical Delrin specimen holders. Each holder has a square slotted hole through its length which supports eight 0.1-inch (2.5-mm) thick plate specimens parallel to each other and to the water flow. The specimens are 3/4 inch (19 mm) wide and 6.5 inches (165 mm) long, with square-cut edges. The edges were not tapered so that some turbulence would be generated at the leading edge of the specimens. Various sulfide ion and ferrous ion levels can be established in each test section independently by means of the injection pumps. Associated with each test section, cylindrical electrodes, approximately 3/8 inch (10 mm) in diameter and 2 inches (50 mm) long, made of the test material, were mounted in the water-flow path by means of plastic piping "tees" and connected to a Petrolite automatic corrosion rate meter, model M-1010-C1, manufactured by Petrolite Corporation, Houston, Texas. This device polarizes the electrodes by 10 mV from their freely corroding potential and monitors the resulting current. This current is a measure of the

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[1] Hall, B.N., "Corrosion Problems Arising in Naval Ships," Corrosion Prevention and Control, Vol. 10, No. 6, pp. 49-52 (June 1963)

*Definitions of abbreviations used are given on page i.

instantaneous corrosion rate of the electrode. If the current values for anodic and cathodic polarization are roughly equal, general corrosion is occurring. If the anodic current is signivicantly greater than the cathodic current, theory states that localized corrosion is occurring. The flow velocity across these electrodes was on the order of 4 ft/s (1.2 m/s) due to the larger cross-sectional area, and turbulent due to the use of the tee.

After exposures in a modified seawater environment in the MSWTL, the specimens and electrodes were transferred to the Alternate Seawater Test Loop, which is similar in construction to the MSWTL but without injection apparatus. There they were exposed to fresh flowing seawater at the same velocities as in the MSWTL for an additional 60 days.

Although ambient sulfide ion concentrations in the seawater entering the MSWTL and ASWTL were less than 0.001 ppm, the ambient ferrous ion levels were of a low but significant level, probably because iron piping was used to supply water to the loops. Background levels of ferrous ions ranged from 0.08 to 0.49 ppm, with an average value of 0.17 ppm during the first run. The average ferrous ion concentrations during the second, third, and fourth runs were 0.09, 0.20, and 0.18 ppm, respectively.

EXPERIMENTAL PROCEDURE

Four different ferrous sulfate treatment sequences were used on 90-10 copper-nickel specimens. The sequences tested were:

- Run 1 - ferrous sulfate treatment (2 hr/day for 14 days)⟶sulfide exposure (continuously for 5 days).
- Run 2 - sulfide exposure (continuously for 5 days)⟶ferrous sulfate treatment (2 hr/day for 14 days).
- Run 3 - ferrous sulfate treatment (2 hr/day for 14 days) + sulfide exposure (continuously for 14 days).
- Run 4 - ferrous sulfate treatment (continuously for 14 days) + sulfide exposure (continuously for 14 days).

70-30 copper nickel specimens were tested only in the first two sequences.

In each run, levels of ferrous sulfate were used which were sufficient to establish ferrous ion levels in the seawater in different portions of the loop of 1.0 and 5.0 ppm. In another section of the loop no ferrous sulfate was injected for one set of specimens, but these specimens still experienced the low background ferrous ion concentration. The level of sulfide used in the tests was 0.2 ppm, with a set of controls being tested with no sulfide injection. This level of sulfide was chosen as being representative of a high-concentration transient experienced in the harbor. Normal sulfide levels in the harbor are on the order of 0.003 ppm.

After the treatment sequences the specimens were placed in the ASWTL where they were run in fresh seawater (no sulfide but background ferrous ion levels) for about 60 days. All specimen exposures were at a flow velocity of 8 ft/s (2.5 m/s). A set of instantaneous corrosion rate electrodes of each material was exposed concurrently with the specimens to the same sequence of environments as the 90-10 copper-nickel specimens. Thus, the last two sequences were run with 70-30 copper-nickel electrodes but not with 70-30 specimens. All electrode exposures were at a flow velocity of 4 ft/s (1.2 m/s).

After exposure, corrosion rate data were obtained by weight loss measurements for the specimens and electrodes. Maximum thickness loss of the specimens was obtained by pit depth measurements. Instantaneous corrosion rate data of the electrodes were obtained concurrently with the exposures.

SPECIMEN RESULTS

Specimen results are reported in table 1 and are represented graphically in figures 2-9. Each bar in the figures represents only two specimens, and the variability between these specimens is sometimes large. A considerable scatter in data is present, and the positions of the bars should be used only to indicate trends, not exact values. Both corrosion rate and thickness loss data are presented, and it is emphasized that neither form of analysis should be used alone to draw conclusions, since an effective inhibitor should reduce both.

TABLE 1
CORROSION DATA FROM SPECIMENS IN TESTS OF FERROUS SULFATE AS A CORROSION INHIBITOR FOR SULFIDE-ACCELERATED ATTACK

		90-10 Alloy				70-30 Alloy			
		$S^{=}$ Level, ppm							
		0.0	0.2	0.2	0.2	0.0	0.2	0.2	0.2
		Fe^{++} Level, ppm							
		Background	Background	1.0	5.0	Background	Background	1.0	5.0
Run 1: $FeSO_4$ (2 hr/day, 14 days → $S^{=}$ (5 days) → SW (60 days)	Corrosion rate, mils/yr (μm/yr)	2.1(55) 2.2(55)	6.2(155) 8.4(215)	5.5(140) 4.1(105)	4.0(100) 6.5(165)	2.8(70) 2.7(70)	6.2(155) 9.0(230)	2.3(60) 1.2(30)	0.5(15) 0.5(15)
	Maximum loss thickness mils (μm)	5(130) 7(180)	12(300) 23(580)	23(580) 11(280)	20(510) 12(300)	4(100) 4(100)	9(230) 18(460)	9(230) 13(330)	12(300) 10(250)
Run 2: $S^{=}$ (5 days) → $FeSO_4$ (2 hr/day, 14 days → SW (60 days)	Corrosion rate, mils/yr (μm/yr)	2.6(65) 2.6(65)	12.6(320) 13.9(355)	8.9(225) 5.7(145)	7.4(190) 6.3(160)	3.3(85) 3.8(95)	11.8(300) 11.5(290)	7.2(185) 5.8(145)	4.9(125) 5.3(135)
	Maximum loss thickness, mils (μm)	1(30) 2(50)	30(1020) 21(530)	4(100) 11(280)	22(560) 17(430)	5(130) 6(150)	8(200) 8(200)	6(150) 5(130)	5(130) 4(100)
Run 3: $FeSO_4$ (2 hr/day, 14 days) + $S^{=}$ (14 days) → SW (60 days)	Corrosion rate, mils/yr (μm/yr)	2.4(60) 2.4(60)	10.0(255) 10.8(275)	9.2(235) 6.4(160)	4.7(120) 3.8(95)				
	Maximum loss thickness, mils (μm)	4(100) 6(150)	16(400) 22(550)	15(380) 12(300)	47(1200) 16(400)				
Run 4: $FeSO_4$ (continuously, 14 days) + $S^{=}$ (14 days) → SW (60 days)	Corrosion rate, mils/yr (μ/yr)	3.0(75) 3.0(75)	7.5(195) 8.5(220)	4.6(115) 2.7(70)	0.8(20) 0.8(20)				
	Maximum loss thickness mils (μm)	3(80) 3(80)	18(460) 7(180)	6(150) 9(230)	3(80) 1(30)				

The large variation in specimen data was caused primarily by the presence of seaweed and other organic matter which became draped over the leading edge of some of the specimens due to inadequate filtering of the seawater. This organic matter introduced turbulence and velocity gradients into the test which were not a part of the original design.

Figures 2 and 3 present the corrosion rate and thickness loss data, respectively, for the first run where the sulfide exposure was preceded by the intermittent ferrous sulfate treatment. Thus, the data in these figures should indicate the ability of ferrous sulfate in preventing sulfide-induced attack. The difference between the control specimens and the background ferrous ion specimens (no treatment) indicates that sulfide-accelerated attack is taking place on all specimens that were not treated. A highly effective treatment should reduce the attack rate to that of the control specimens.

The corrosion rate of the 70-30 copper-nickel is reduced to that of the control specimens by both levels of ferrous sulfate, but the maximum pit depth is not reduced, indicating that the effect of the inhibitor treatment is to reduce the number of pits but not their depth. The inhibitor somewhat reduced the corrosion rate of 90-10 copper-nickel but had no effect on the pit depth.

Figures 4 and 5 present corrosion rate and thickness loss data, respectively, for the second run where the sulfide exposure preceded the intermittent ferrous sulfate treatment. Thus, these data should indicate the ability of the ferrous sulfate in countering the sulfide-accelerated attack once it has initiated.

The corrosion rate of 70-30 copper-nickel is reduced almost to the level of the controls, and the pit depth data for this alloy also indicate a reduction. The data for 90-10 copper-nickel indicate a partial reduction in corrosion rate but no significant reduction in pit depth.

Figures 6 and 7 present the data for the third run where sulfide exposure was conducted concurrently with the ferrous sulfate treatment. It should be noted that the length of sulfide exposure in this and the following run was 14 days. This exposure period made it possible to have sulfide present during the entire time that the material was exposed to the $FeSO_4$.

90-10 copper-nickel experienced some reduction in corrosion rate by the use of inhibitor 2 hours per day, but the treatment had no effect on pit depth.

The last run, for which data are presented in figures 8 and 9, included sulfide exposure and continuous inhibitor treatment, applied simultaneously. Both the corrosion rates and the pit depths of 90-10 copper nickel were reduced to the control levels by the inhibitor treatment, but the 5.0 ppm ferrous ion level was necessary for complete suppression of the sulfide-accelerated corrosion.

During the fourth run a sludge of ferric hydroxide was deposited in the test loop. When the ferrous sulfate injection was begun, the concentration of sulfide was immediately reduced by greater than an order of magnitude. It is therefore reasonable to assume that the highly beneficial effect of continuous ferrous sulfate treatment is due primarily to its ability to strip the corrosion-accelerating sulfides from solution and not from any direct corrosion-inhibition effects.

ELECTRODE RESULTS

CORROSION RATE DATA

Corrosion data for the instantaneous corrosion rate electrodes are presented in table 2 and in figures 10-13. In figure 10 it can be seen that the sulfide-induced corrosion of 70-30 copper-nickel electrodes was completely prevented by treatment with the higher concentration of ferrous sulfate. Sulfide-accelerated corrosion of the 90-10 copper-nickel electrodes was prevented by treatment at the lower concentration as well.

Figure 11 indicates that the inhibitor treatment was less effective in countering the sulfide-induced corrosion once it had initiated. The corrosion rates were not reduced to the level of the controls by the inhibitor treatment, although the rate of the 90-10 copper-nickel electrodes did come close.

The third treatment scheme, as indicated in figure 12, had about the same effect as the second treatment scheme, with only partial reduction in corrosion rate of the 70-30 copper-nickel electrodes and almost complete reduction in the rates of the 90-10 copper-nickel electrodes to those of the controls.

As illustrated in figure 13, continuous application of ferrous sulfate at either concentration totally reduced the corrosion rate of the electrodes of either alloy to the control level. As with the specimens, this result could be due primarily to the stripping of sulfides from solution and not from true inhibition effects.

TABLE 2
CORROSION DATA FROM ELECTRODES IN TESTS
OF FERROUS SULFATE AS A CORROSION INHIBITOR
FOR SULFIDE-ACCELERATED ATTACK

		90-10 Alloy				70-30 Alloy			
		$S^=$ Level, ppm							
		0.0	0.2	0.2	0.2	0.0	0.2	0.2	0.2
		Fe^{++} Level,							
		Background	Background	1.0	5.0	Background	Background	1.0	5.0
Run 1: $FeSO_4$ (2 hr/day, 14 days) → $S^=$ (5 days) → SW (60 days)	Average corrosion rate, mils/yr (μm/yr)	2.1(55)	2.3(60)	1.2(30)	0.7(20)	0.8(20)	4.3(110)	1.4(35)	0.4(10)
	Average instantaneous corrosion rate mils/yr (μm/yr) Anodic	3.8(95)	8.9(225)	1.9(50)	1.8(45)	1.0(25)	13.7(350)	5.7(145)	0.9(25)
	Cathodic	2.6(65)	5.8(145)	1.7(45)	1.3(35)	1.0(25)	11.1(280)	3.8(95)	0.7(20)
Run 2: $S^=$ (5 days) → $FeSO_4$ (2 hr/day, 14 days) → SW (60 days)	Average corrosion rate, mils/yr (μm/yr)	2.4(60)	7.0(180)	4.4(110)	2.8(70)	0.9(25)	4.9(125)	3.3(85)	2.9(75)
	Average instantaneous corrosion rate mils/yr (μm/yr) Anodic	4.1(105)	21.6(550)	16.7(425)	9.7(245)	1.0(25)	16.7(425)	13.6(345)	12.4(315
	Cathodic	3.1(80)	19.1(485)	13.4(340)	5.2(130)	0.8(20)	12.8(325)	9.7(245)	8.1(205)
Run 3: $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (14 days) → SW (60 days)	Average corrosion rate, mils/yr (μm/yr)	1.7(45)	4.5(110)	3.0(75)	1.9(50)	1.1(30)	3.6(90)	3.5(90)	2.9(75)
	Average instantaneous corrosion rate mils/yr (μm/yr) Anodic	2.5(65)	12.3(310)	10.6(270)	7.4(190)	1.8(45)	14.4(365)	14.3(360)	11.0(280)
	Cathodic	1.9(50)	9.1(230)	7.2(185)	4.6(115)	1.5(40)	10.1(260)	9.5(240)	6.2(155)
Run 4: $FeSO_4$ (continusouly 14 days) + $S^=$ (14 days), → SW (60 days)	Average corrosion rate, mils/yr (μm/yr)	2.5(65)	4.2(105)	1.1(30)	0.8(20)	1.2(30)	3.0(75)	0.7(20)	0.5(15)
	Average instantaneous corrosion rate mils/yr (μm/yr) Anodic	4.3(110)	9.4(240)	3.0(75)	2.2(55)	2.3(60)	11.6(305)	0.7(20)	1.3(30)
	Cathodic	3.1(80)	6.4(160)	1.9(50)	1.4(35)	1.7(45)	7.9(200)	0.6(15)	0.9(25)

INSTANTANEOUS CORROSION RATES

To ensure that the polarization-resistance technique used for these measurements is an accurate method for determining corrosion rates, it was necessary to validate the corrosion rates obtained in this manner against rates obtained on the electrodes by weight loss measurements. Table 2 presents the corrosion rate obtained by weight loss measurements and the average value for the entire test duration of the instantaneous corrosion rate for each electrode set. These rates are plotted against each other in figure 14, for both alloys. In addition, data are plotted from a concurrent study which will be reported in detail at a later time.

A linear regression analysis of the data was used to generate the best-fit line and the 70% confidence limits shown in the figure. Analysis for the correlation coefficient R yields a value of 0.84, indicating that a good correlation exists between the average instantaneous corrosion rate and the rate obtained by weight loss data. It is therefore reasonable to use instantaneous corrosion rate to predict trends in corrosion activity. However, since enough scatter is present to give a standard deviation $S_{y,x}$ of 1.7 times the data value, it is not feasible to use instantaneous corrosion rate data for predicting exact corrosion rate values.

The instantaneous corrosion rates for the 70-30 copper-nickel electrodes are plotted in figures 15 through 18. Figure 15 illustrates that the sulfide-induced corrosion peak of 70-30 copper-nickel electrodes is partially prevented by the low concentration inhibitor treatment and is completely prevented by the high concentration treatment. The data in figure 16 indicate that either level of inhibitor treatment only partially countered the sulfide-induced attack once this attack had started. Inhibitor treatment at the low concentration had only minimal influence on the corrosion of 70-30 copper-nickel in the third run where intermittent $FeSO_4$ is added during sulfide exposure, as illustrated in figure 17. The higher concentration, although causing some initial reduction, only minimally reduced the corrosion during the rest of the test. Results of the fourth run, plotted in figure 18, indicate that either concentration of inhibitor, when added continuously, eliminated the sulfide-induced corrosion peak of the 70-30 copper-nickel electrodes. In all of the runs there was no systematic effect of inhibitor concentration or sulfide on the corrosion potential of the electrodes.

Plots of the instantaneous corrosion rates of the 90-10 copper-nickel electrodes versus time in test are presented as figures 19 through 22. In figure 19 it can be seen that the peak in corrosion rate of 90-10 copper-nickel, caused by the sulfide injection, is completely prevented by the use of the inhibitor. In figure 20 the higher concentration of inhibitor appears to have completely countered the effect of the sulfide after 6 days of use, whereas the lower concentration of inhibitor took longer to act and was not as effective. The results of the third run, presented as figure 21, indicate partial reduction of the sulfide-induced corrosion peak by the lower inhibitor concentration and total reduction by the high inhibitor concentration. Both concentrations greatly reduced the sulfide-induced corrosion in the fourth run, as illustrated in figure 22. No systematic influence of inhibitor on the corrosion potentials in any of the runs could be found. Potentials of the 90-10 copper-nickel electrodes that were exposed to sulfide without inhibitor were generally 100-150 mV more electropositive than those of the electrodes that were exposed to seawater containing no sulfide.

Generally, the ferrous sulfate inhibitor treatments caused greater reduction in sulfide-induced corrosion on the electrodes than on the specimens. This was most obvious when considering the instantaneous corrosion rates. In addition, the amount of sulfide-induced pitting on the electrodes was too low to justify recording maximum pit depth measurements. These differences were most likely due to the difference in flow characteristics at the two locations, although material differences could be a contributing cause. The velocity across the electrodes was only half that across the specimens, and the turbulence at the two locations was different. Therefore, the amount of sulfide-induced attack and the effect of ferrous sulfate inhibitor on this attack appear in this study to be related to flow velocity and turbulence.

DISCUSSION AND RECOMMENDATIONS

The effects of the various ferrous sulfate treatments on the corrosion rates and pit depths of the 90-10 and 70-30 copper-nickel alloys are summarized in table 3. Any evaluation of the overall effectiveness of each treatment scheme on each alloy should be heavily weighted toward the specimen maximum thickness loss data, since the primary mode of the service failures has been by penetration by discrete pits.

TABLE 3
SUMMARY OF THE AMOUNT OF REDUCTION OF SULFIDE-ACCELERATED CORROSION OF COPPER-NICKELS BY VARIOUS INHIBITOR TREATMENTS*

		Specimen 8 ft/s (1.6 m/s)				Electrodes 4 ft/s (1.2 m/s)			
		90-10 Cu-Ni Alloy		70-30 Cu-Ni Alloy		90-10 Cu-Ni Alloy		70-30 Cu-Ni Alloy	
		Fe^{++} Level, ppm							
		1.0	5.0	1.0	5.0	1.0	5.0	1.0	5.0
Run 1: $FeSO_4$ (2hr/day, 14 days) → $S^=$ (5 days) → SW (60 days)	Weight loss corrosion rate	P	P	C	C	C	C	P	C
	Maximum loss thickness (specimens) or instantaneous corrosion rate (electrodes)	N	N	N	N	C	C	P	C
Run 2: $S^=$ (5 days) → $FeSO_4$ (2hr/day, 14 days) → SW (60 days)	Weight loss corrosion rate	P	P	P	P	P	P	P	P
	Maximum loss thickness (specimens) or instantaneous corrosion rate electrodes)	P	N	C	C	P	C	P	P
Run 3: $FeSO_4$ (2hr/day, 14 days) + $S^=$ (14 days) → SW (60 days)	Weight loss corrosion rate	P	P			P	P	N	P
	Maximum loss thickness (specimens) or instantaneous corrosion rate electrodes	N	N			P	C	N	N
Run 4: $FeSO_4$ (continuously 14 days) + $S^=$ (14 days) → SW (60 days)	Weight loss corrosion rate	P	C			C	C	C	C
	Maximum loss thickness (specimens) or instantaneous corrosion rate electrodes)	P	C			C	C	C	C

C = Complete reduction to control levels.
P = Partial reduction to control levels.
N = No reduction.

Generally, pretreatment by the ferrous sulfate inhibitor was not effective in preventing sulfide-accelerated pitting of either alloy. Treatment after sulfide exposure was only partially effective in countering the attack on 90-10 and 70-30 copper-nickel. Intermittent treatment during the continuous sulfide exposure was not effective on either alloy, but continuous treatment during the sulfide exposure was completely effective at both concentrations on 70-30 copper-nickel and at the higher concentration on 90-10 copper-nickel. This benefit was probably due more to the effect of the ferrous sulfate in stripping the sulfide ions from solution than directly to any corrosion-inhibition effect.

Sulfide exposures during these tests were conducted at relatively high levels compared to the normal harbor environment, and for short periods of time to simulate higher level sulfide transients which have been experienced. The effectiveness of the inhibitor as described above is relative to these conditions. An alternate hypothesis concerning the initiation of sulfide-accelerated attack involves a much lower level of sulfide such

as the 0.003 ppm level normally present in the harbor over considerably longer periods of time. The effect of ferrous sulfate inhibitor on sulfide-accelerated attack induced in this manner cannot be assessed from these tests, however, additional tests in seawater with lower sulfide concentrations are in progress.

Continuous ferrous sulfate injection, although the most effective treatment procedure, may be impractical due to the buildup of the ferric hydroxide sludge which could affect heat exchanger performance. Another consideration is that in a single system consisting of nominal 6-inch pipe with a flow velocity of 8 ft/s (2.5 m/s), 200 pounds (100 kg) of inhibitor would be required for 1-day's injection at the 5-ppm ferrous ion level (it takes roughly 25 ppm of ferrous sulfate to establish a level of 5 ppm of ferrous ion in seawater). This would cost roughly $300 per system per day. In addition, continuous addition of this quantity of ferrous sulfate into the harbor may violate EPA regulations.

Intermittent injection is therefore the more practical approach. Less injection equipment is needed since the same equipment can be used on several systems sequentially. Unfortunately, intermittent injection is not as effective as continuous injection in suppressing the accelerated corrosion. The benefits of injection versus the cost must be considered by the shipbuilders in order to assess the suitability of the procedure. It should be emphasized that the information contained in this report is relevant only to inhibition of corrosion caused by transient elevated-level (0.2 ppm) sulfide environments. Intermittent ferrous sulfate injection may be more effective where lower levels of sulfide are encountered during construction.

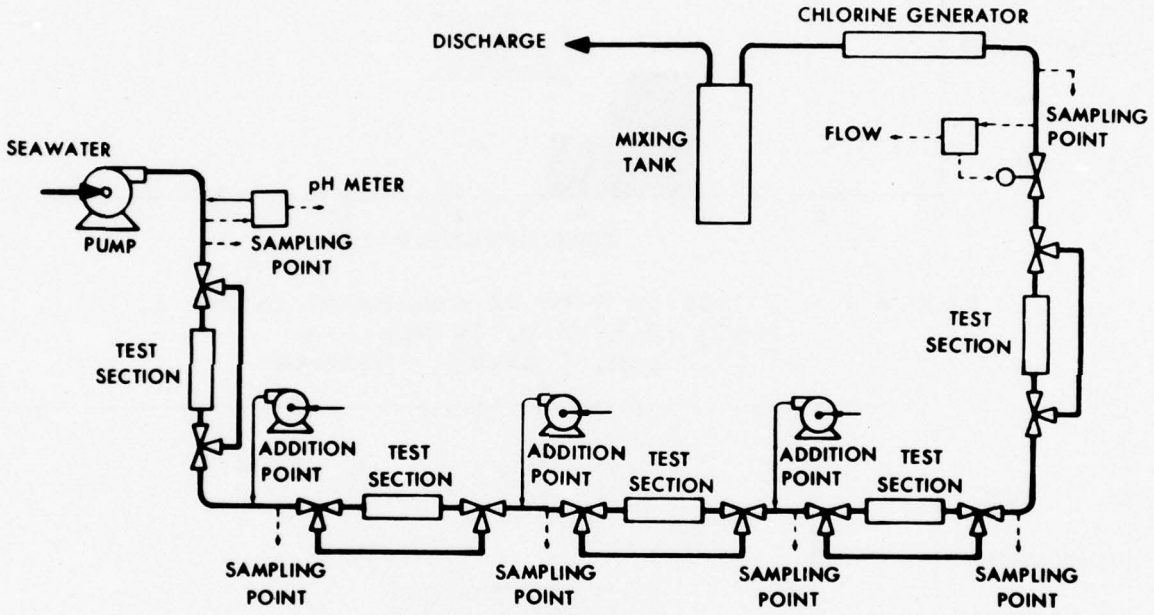

Figure 1 - Modified Seawater Test Loop

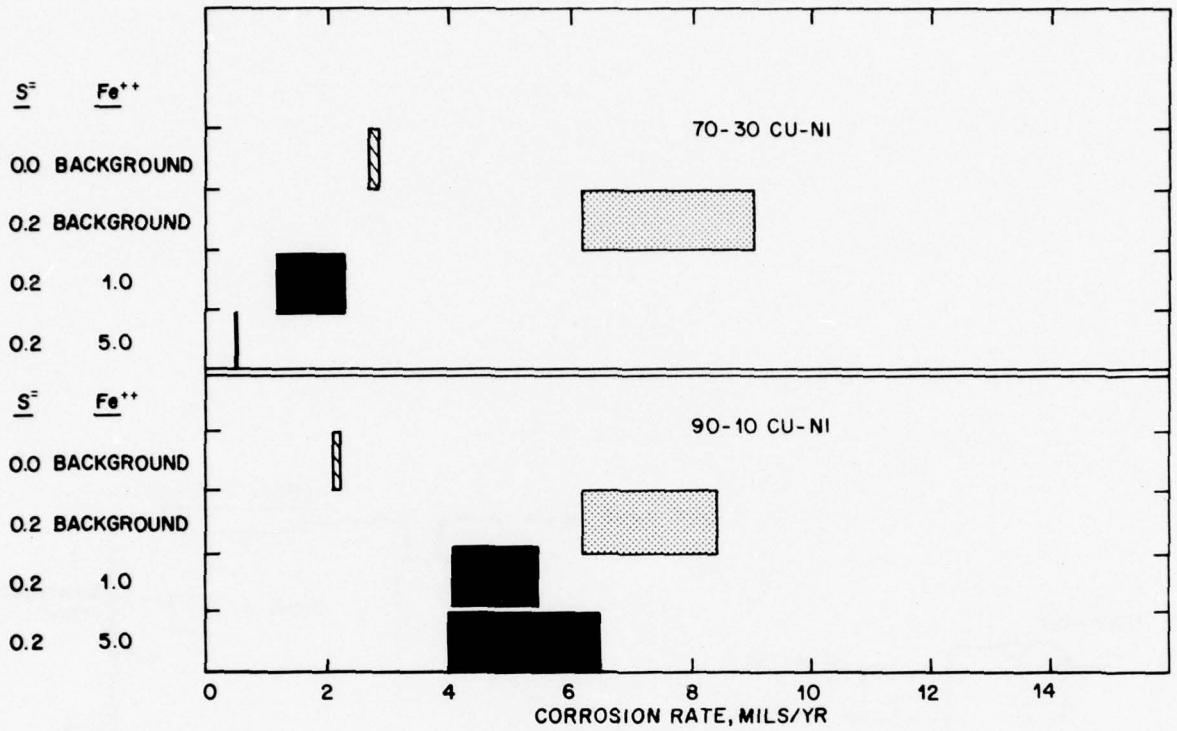

Figure 2 - Corrosion Rate of Specimens in Run 1, $FeSO_4$ (2 hr/day, 14 days) → $S^=$ (0.2 ppm, 5 days) → Seawater

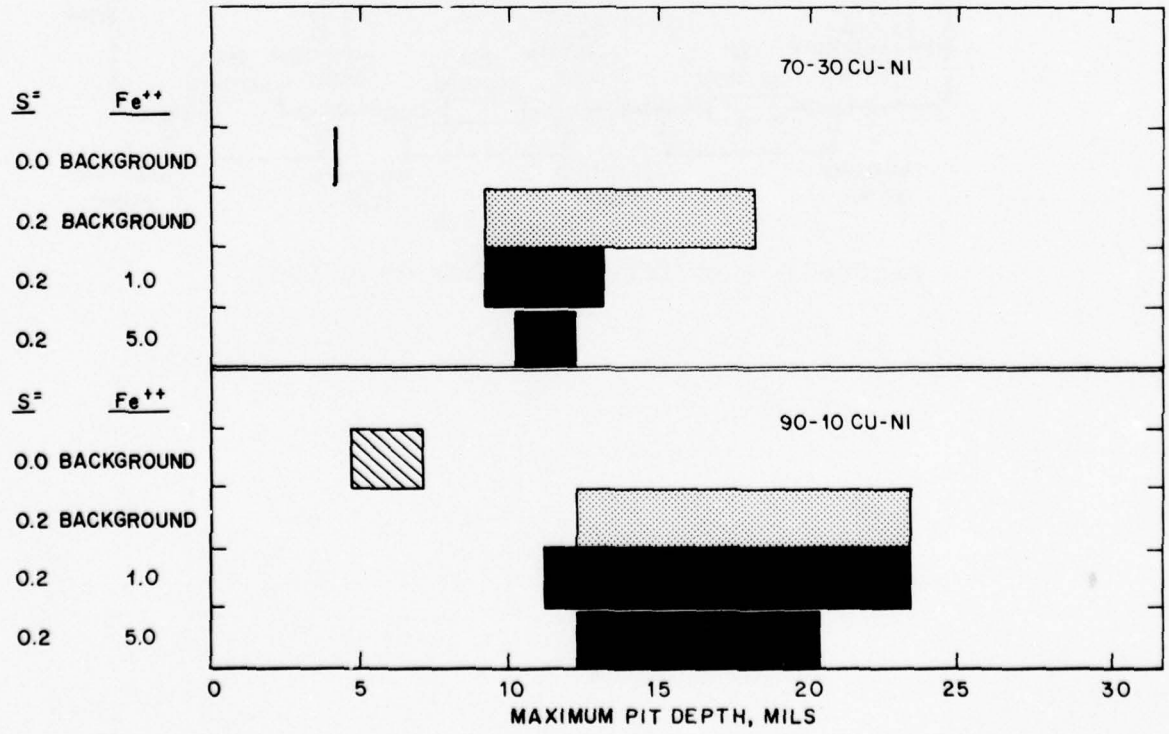

Figure 3 - Maximum Pit Depth of Specimens in Run 1, $FeSO_4$ (2 hr/day, 14 days) → $S^=$ (0.2 ppm, 5 days) → Seawater

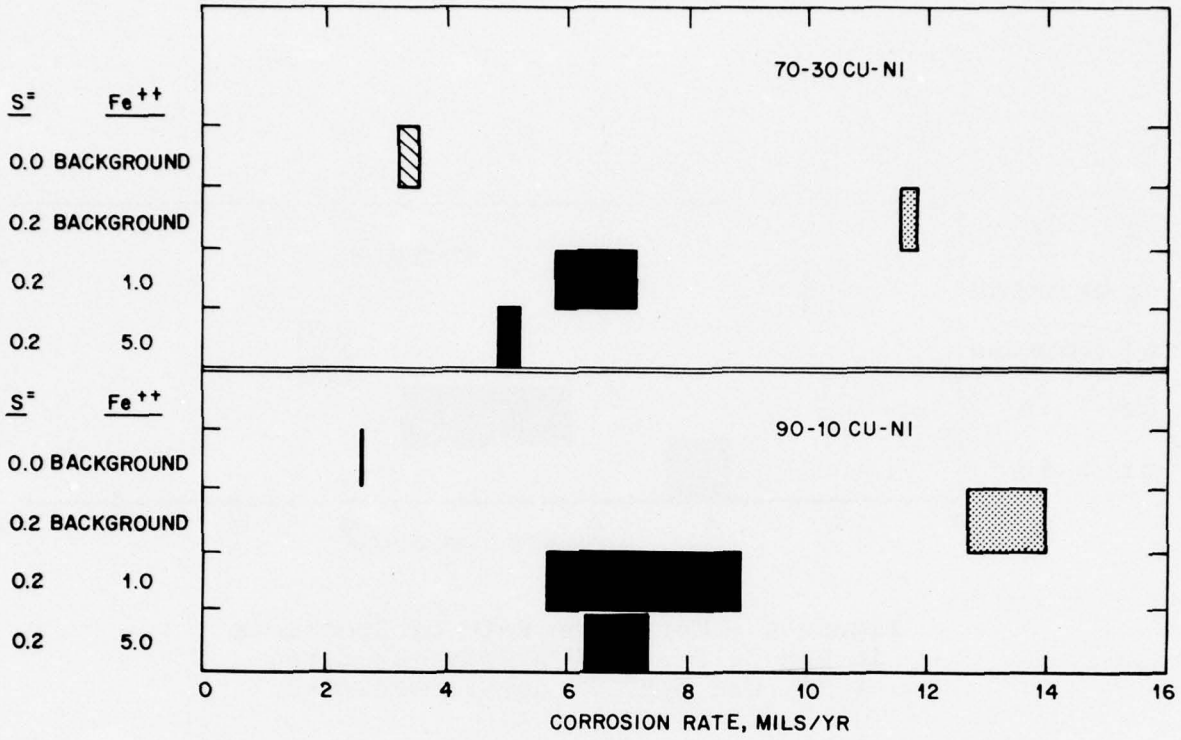

Figure 4 - Corrosion Rate of Specimens in Run 2, $S^{=}$ (0.2 ppm, 5 days) → $FeSO_4$ (2 hr/day, 14 days) → Seawater

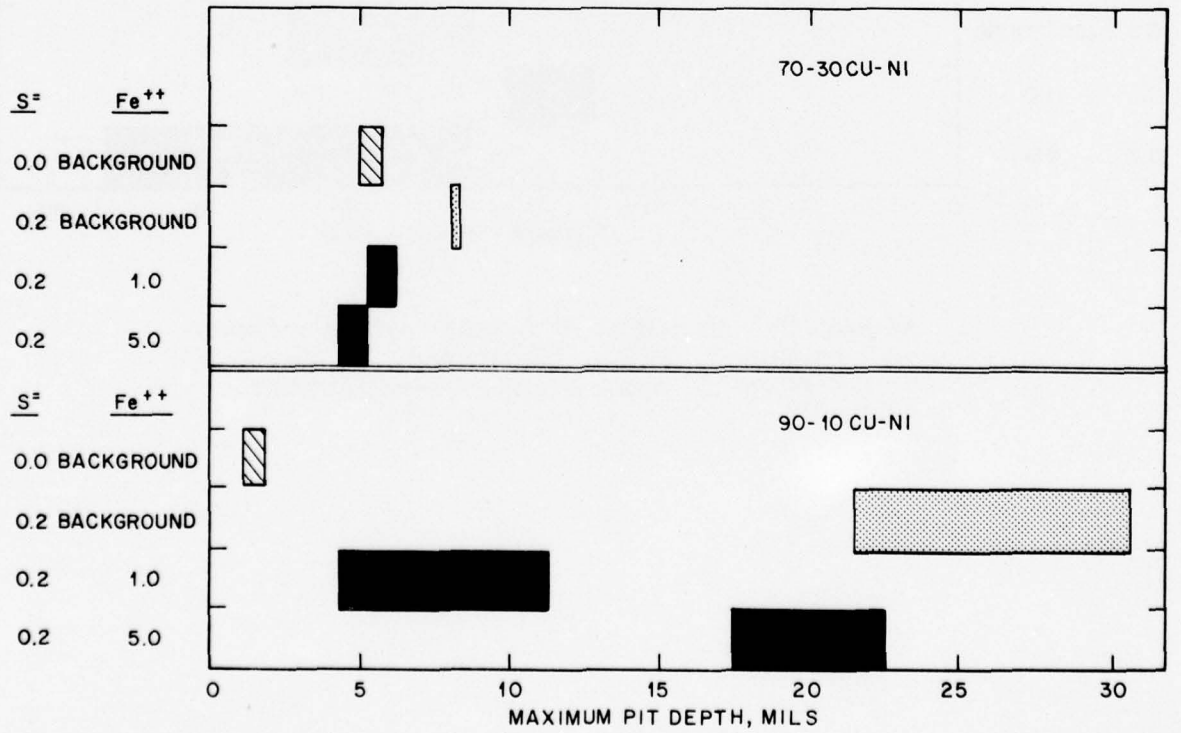

Figure 5 - Maximum Pit Depth of Specimens in Run 2, $S^{=}$ (0.2 ppm, 5 days) → $FeSO_4$ (2 hr/day, 14 days) → Seawater

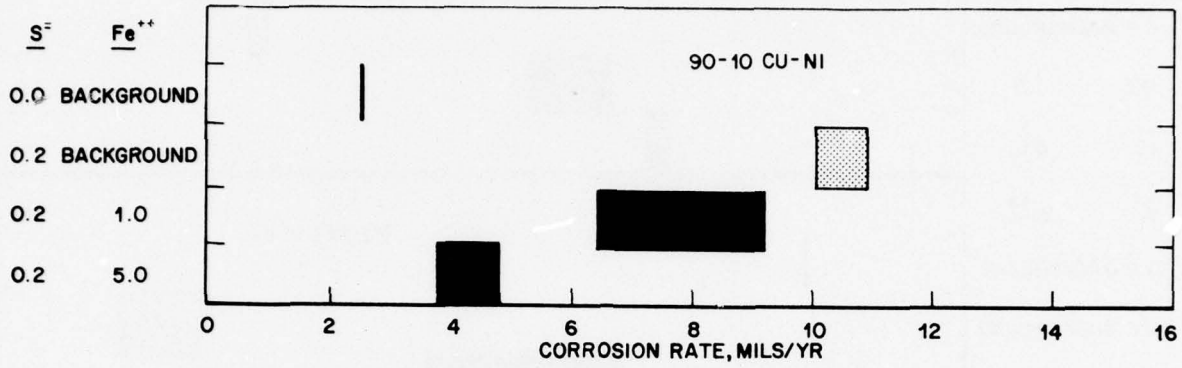

Figure 6 - Corrosion Rate of Specimens in Run 3, $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (0.2 ppm, 14 days)→Seawater

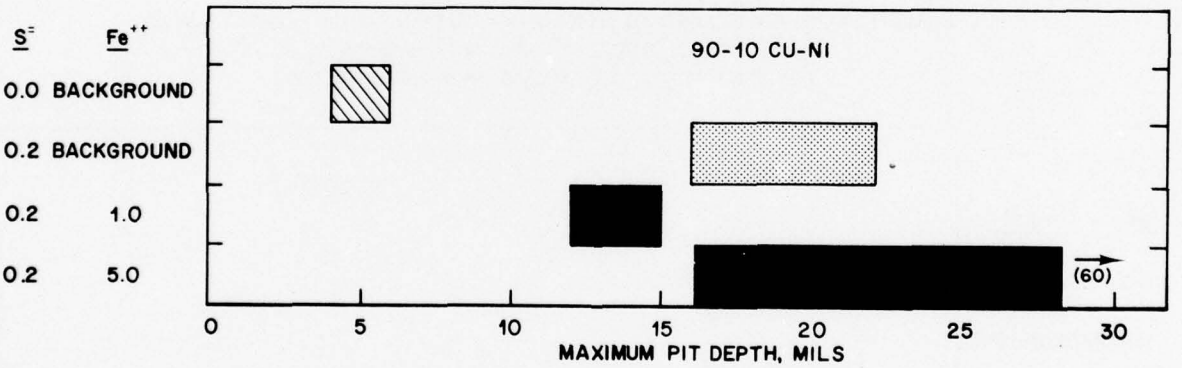

Figure 7 - Maximum Pit Depth of Specimens in Run 3, $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (0.2 ppm, 14 days)→Seawater

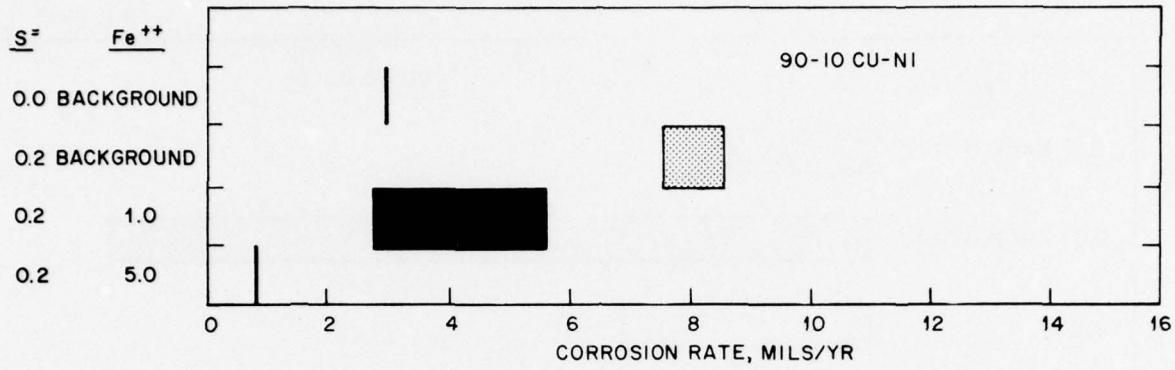

Figure 8 - Corrosion Rate of Specimens in Run 4, $FeSO_4$ (Continuous, 14 days) + $S^=$ (0.2 ppm, 14 days)→Seawater

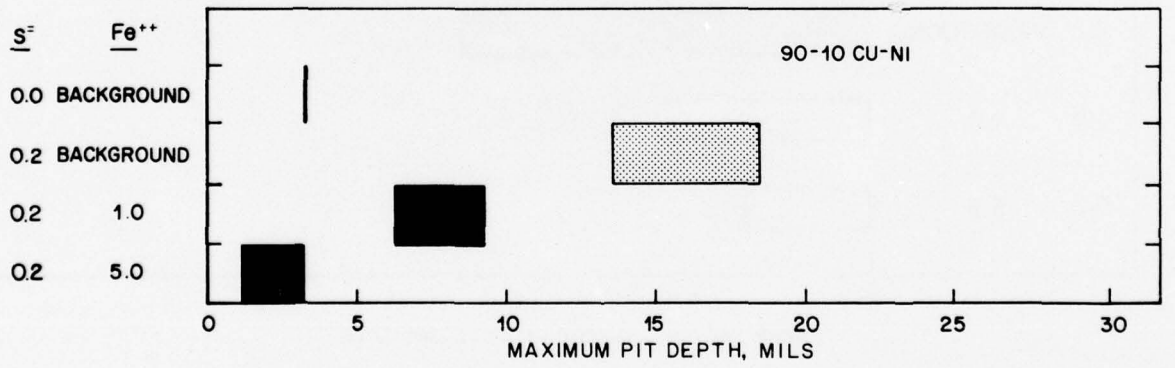

Figure 9 - Maximum Pit Depth of Specimens in Run 4, $FeSO_4$ (Continuous, 14 days) + $S^=$ (0.2 ppm, 14 days)→Seawater

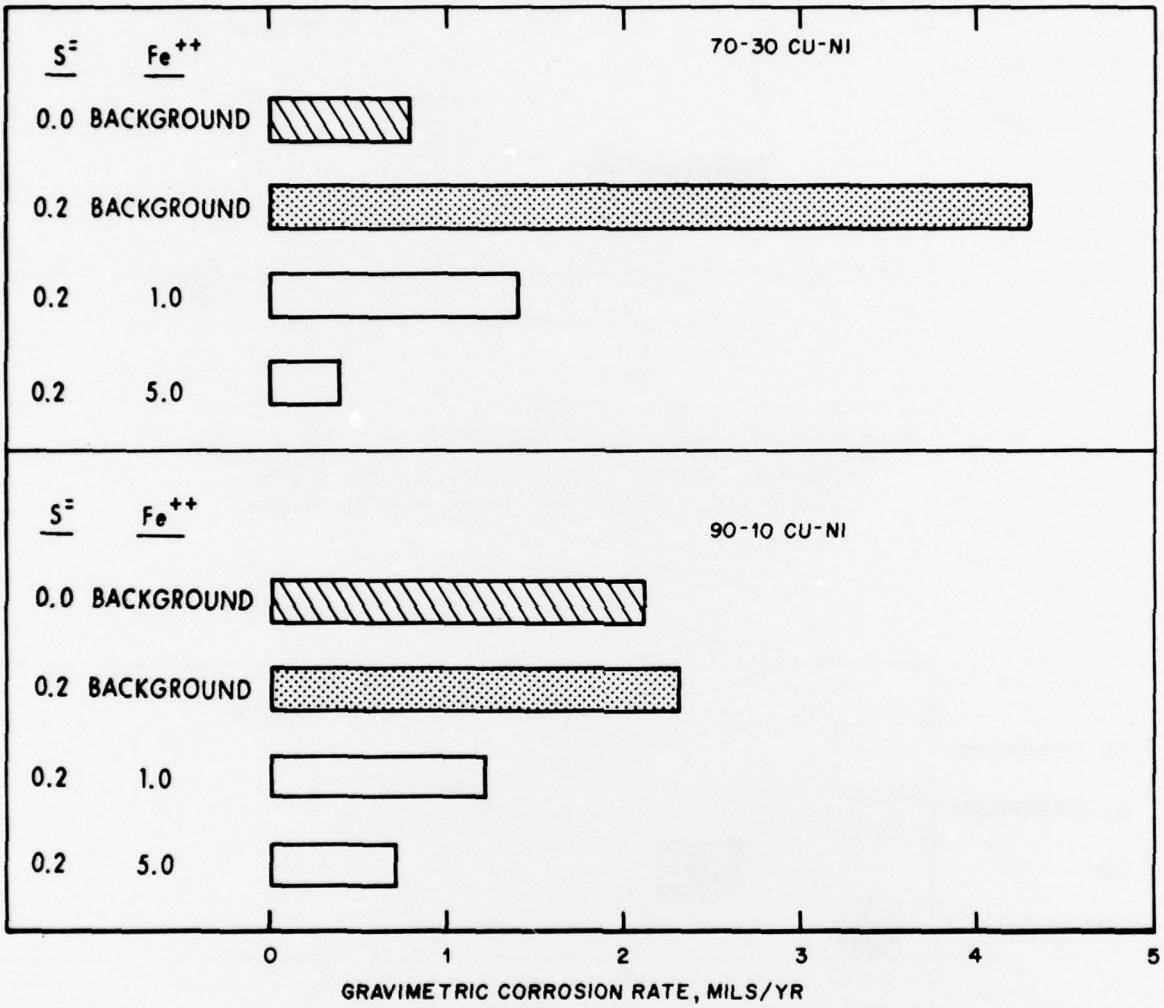

Figure 10 - Average Corrosion Rate of Electrodes in Run 1, $FeSO_4$ (2 hr/day, 14 days) →$S^=$ (0.2 ppm, 5 days)→Seawater

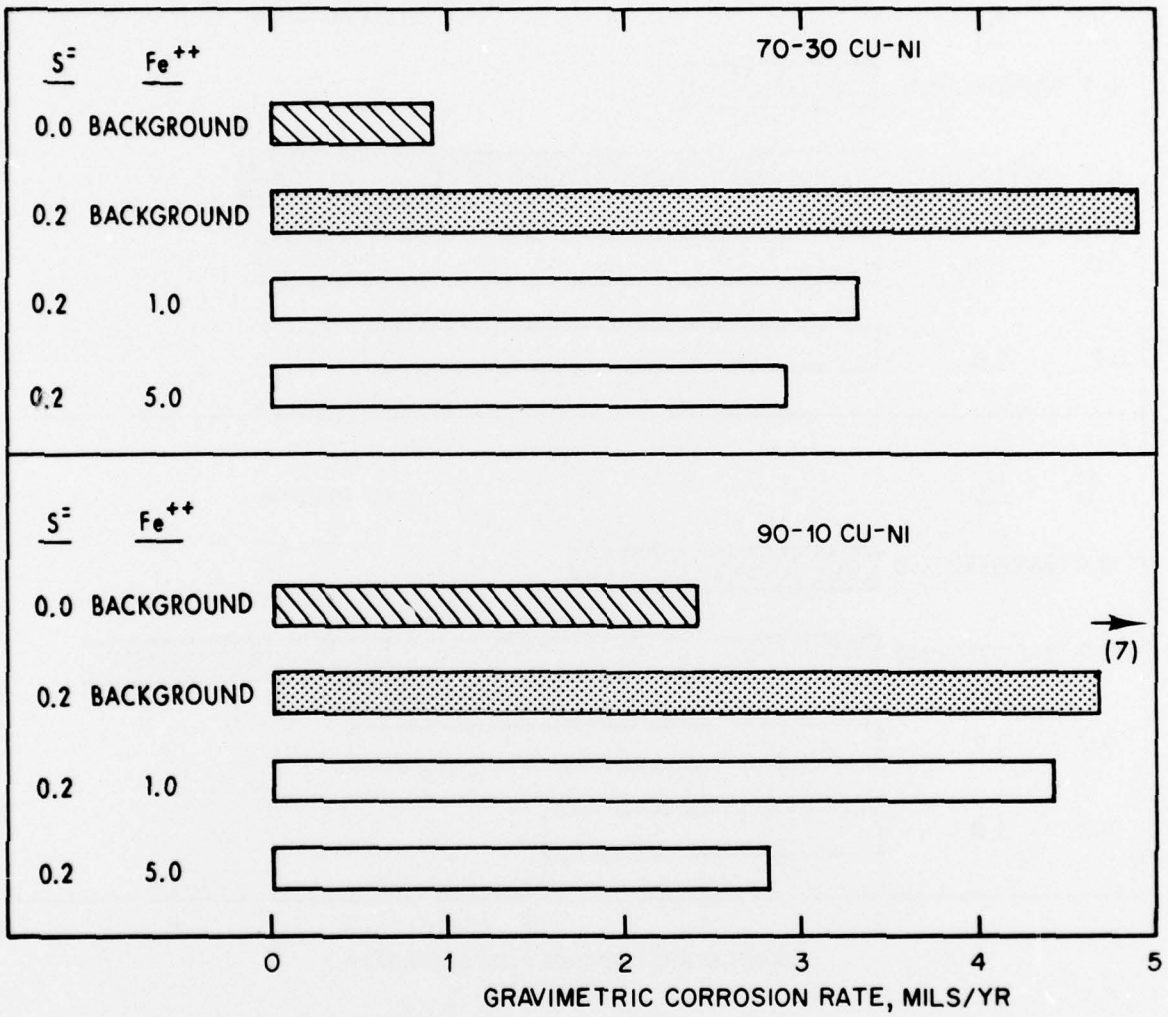

Figure 11 - Average Corrosion Rate of Electrodes in Run 2, $S^=$ (0.2 ppm, 5 days) → $FeSO_4$ (2 hr/day, 14 days) → Seawater

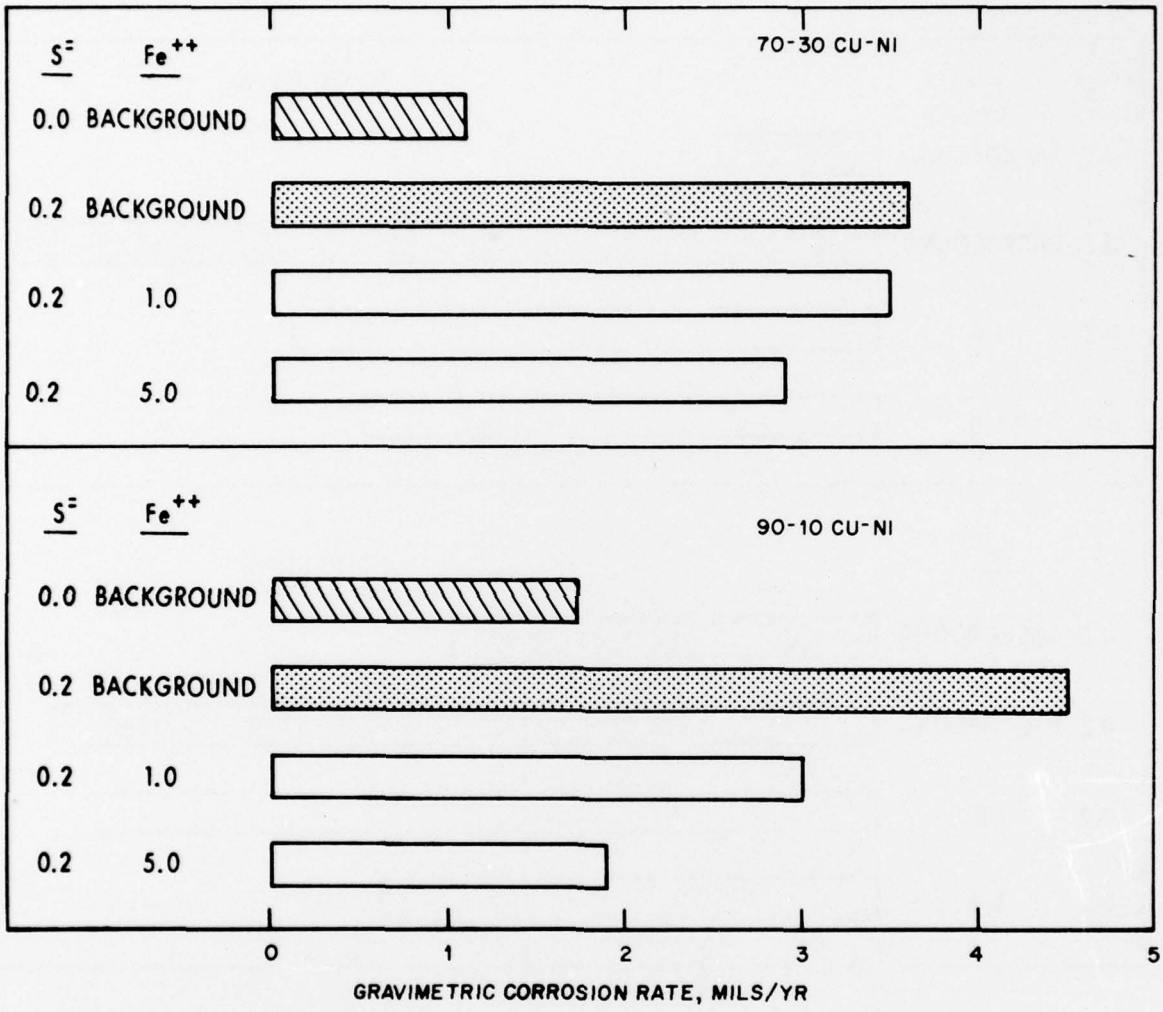

Figure 12 - Average Corrosion Rate of Electrodes in Run 3, $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (0.2 ppm, 14 days) → Seawater

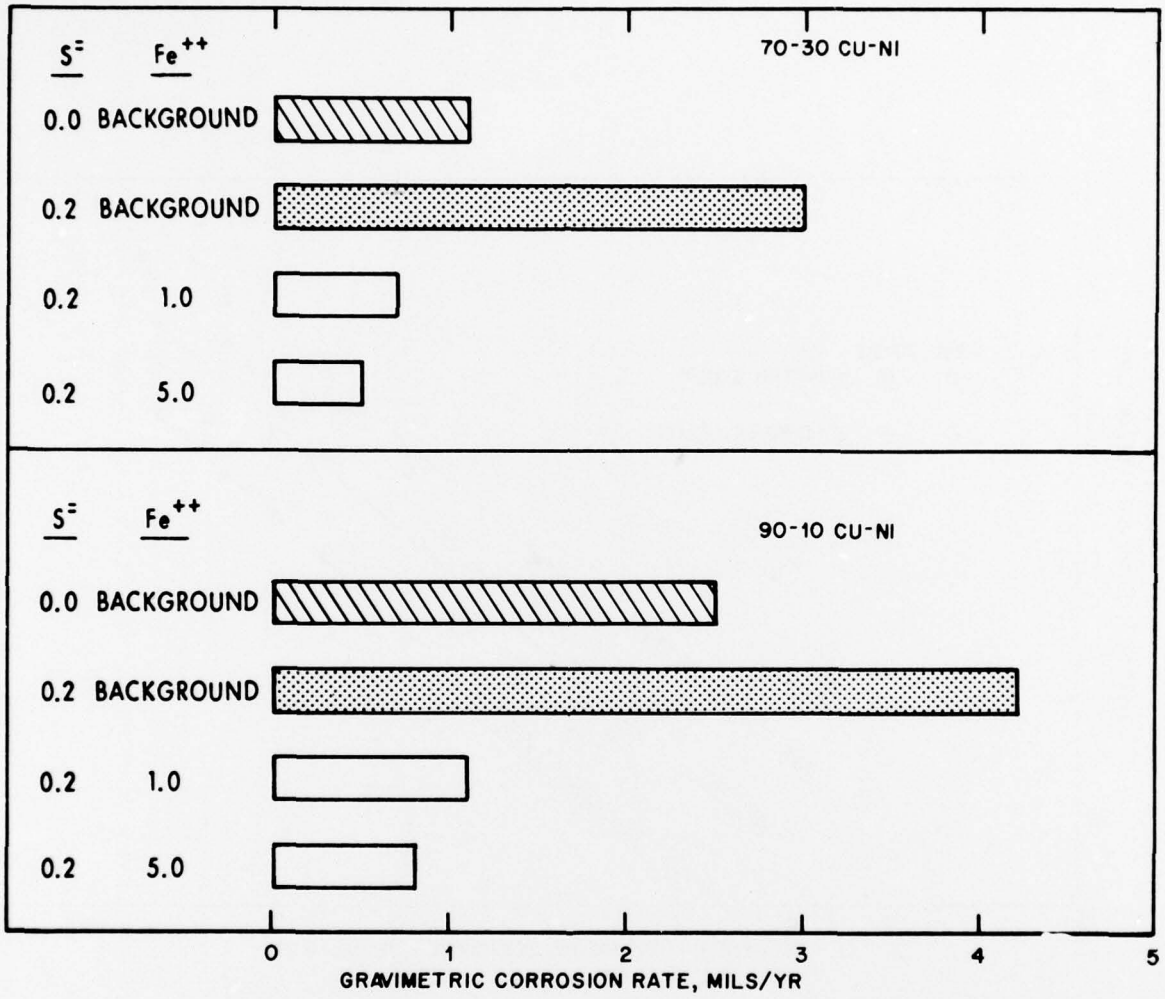

Figure 13 - Average Corrosion Rate of Electrodes in Run 4, $FeSO_4$ (Continuous, 14 days) + $S^=$ (0.2 ppm, 14 days) → Seawater

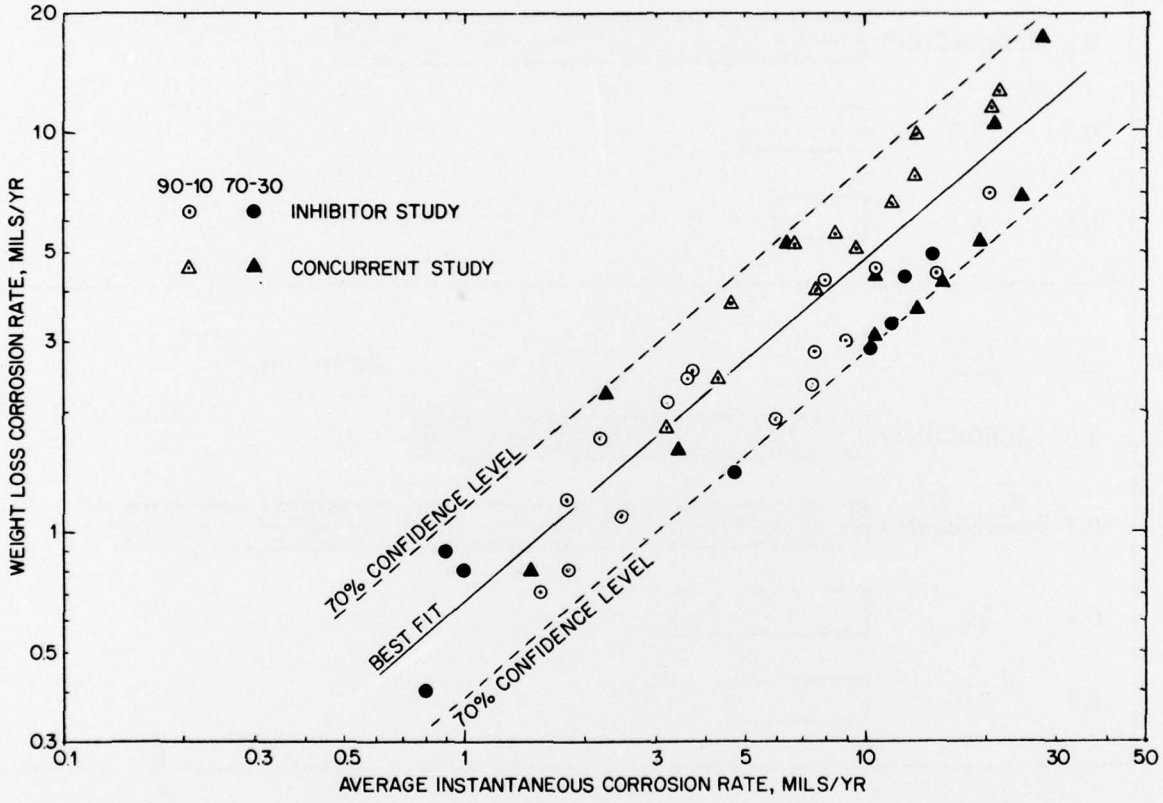

Figure 14 - Correlation of Weight Loss Corrosion Rate with Average Instantaneous Corrosion Rate

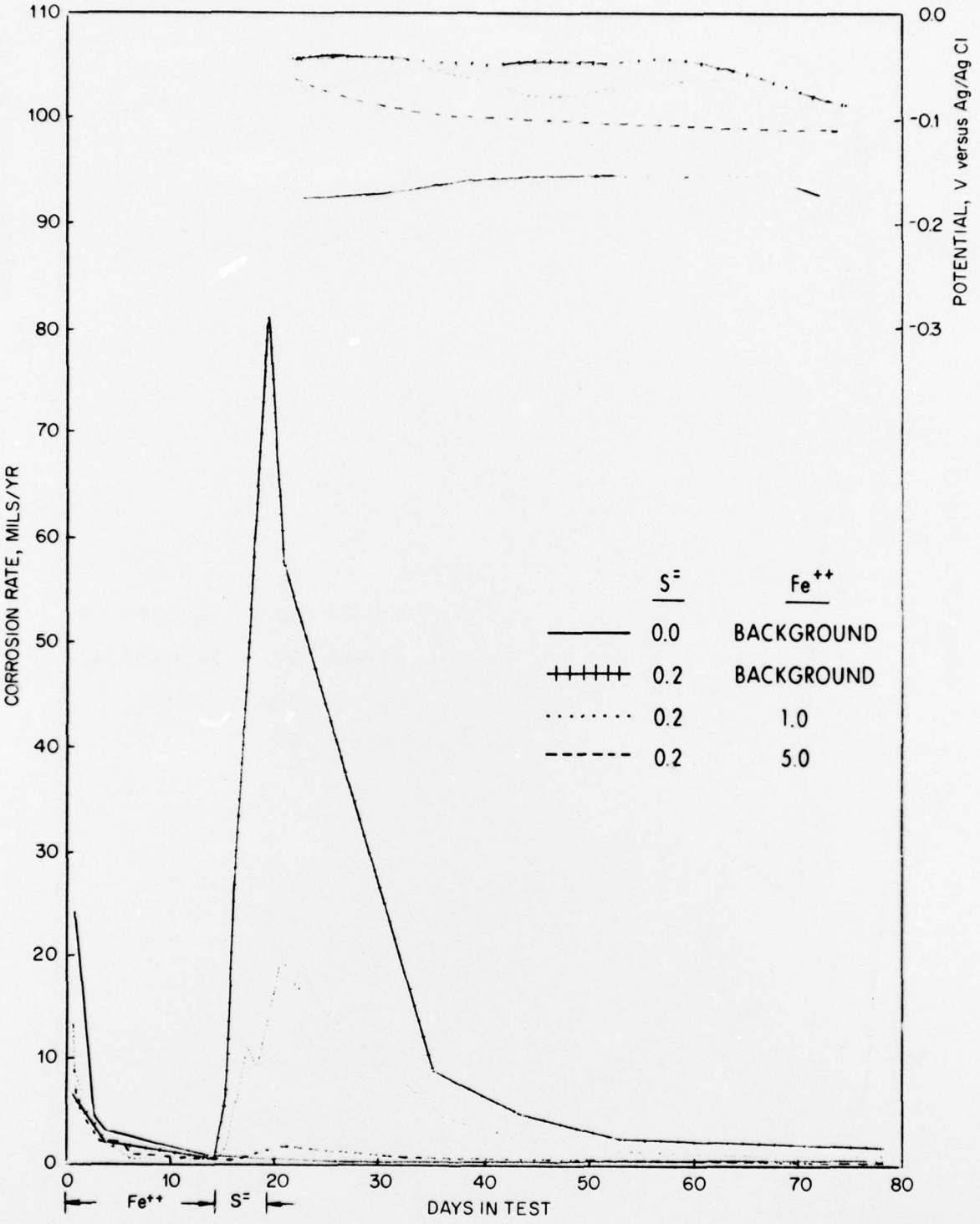

Figure 15 - Instantaneous Corrosion Rate of 70-30 Cu-Ni Electrodes in Run 1, $FeSO_4$ (2 hr/day, 14 days) → $S^=$ (0.2 ppm, 5 days) → Seawater

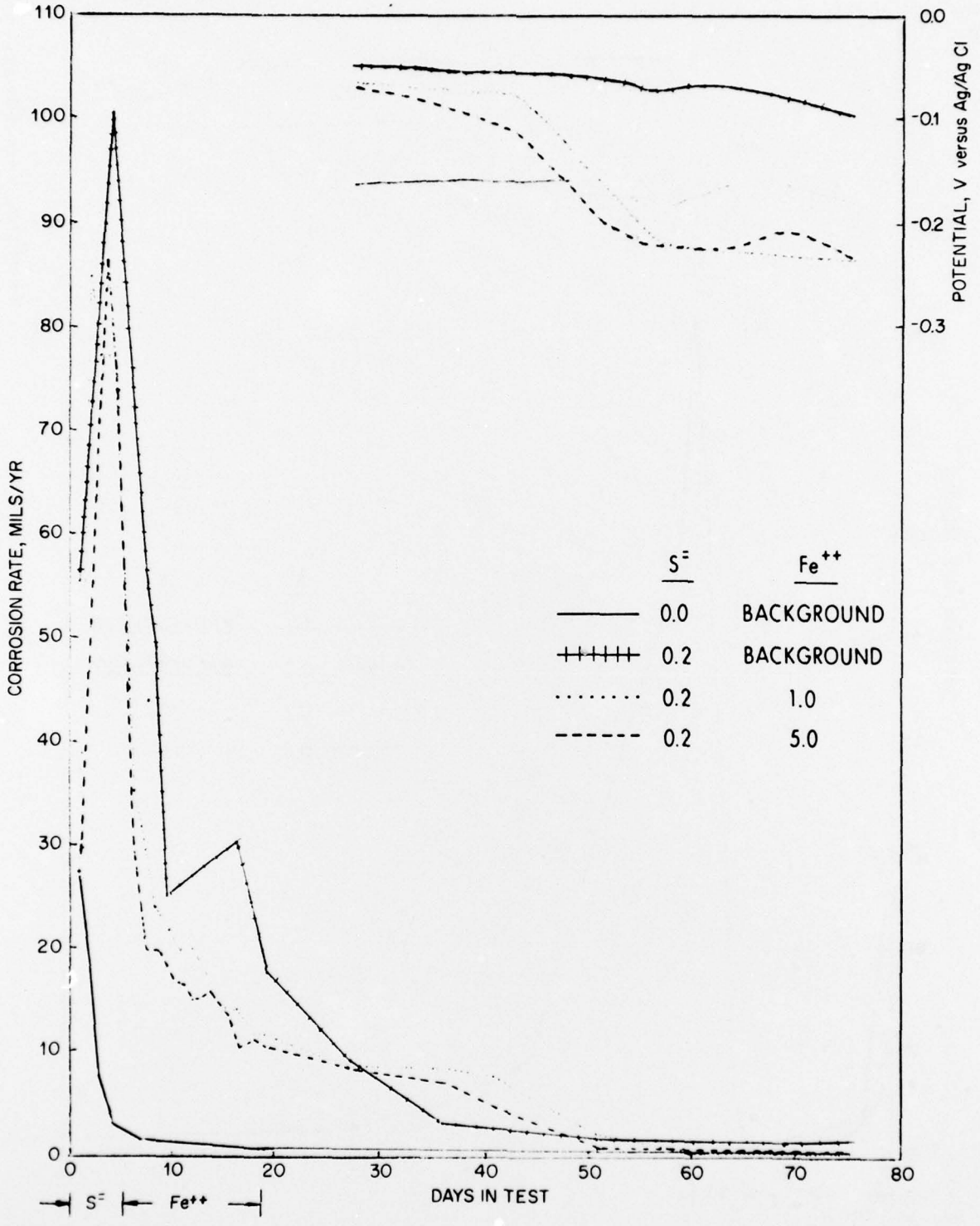

Figure 16 - Instantaneous Corrosion Rate of 70-30 Cu-Ni Electrodes in Run 2, $S^{=}$ (0.2 ppm, 5 days) → FeSO4 (2 hr/day, 14 days) → Seawater

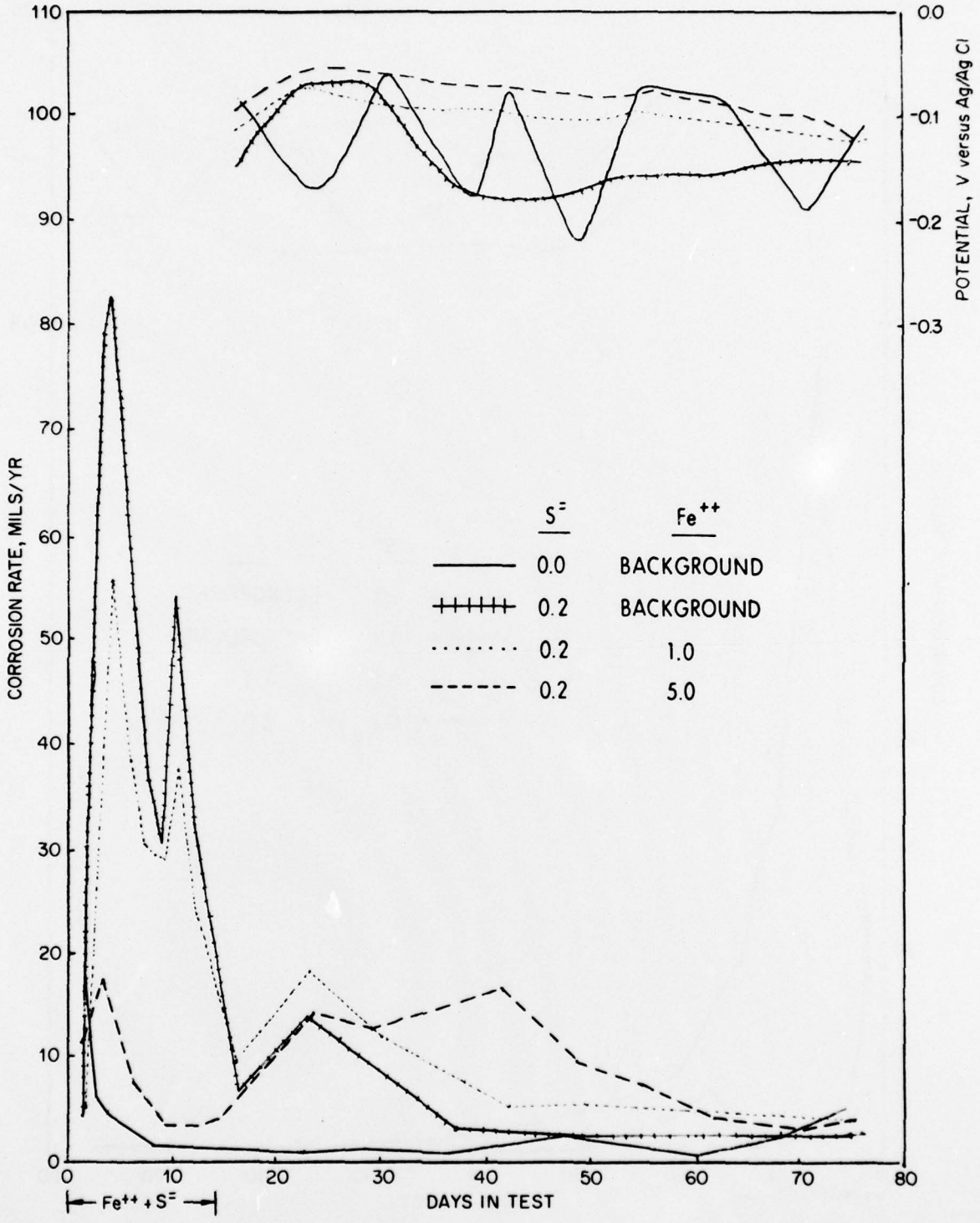

Figure 17 - Instantaneous Corrosion Rate of 70-30 Cu-Ni Electrodes in Run 3, $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (0.2 ppm, 14 days) → Seawater

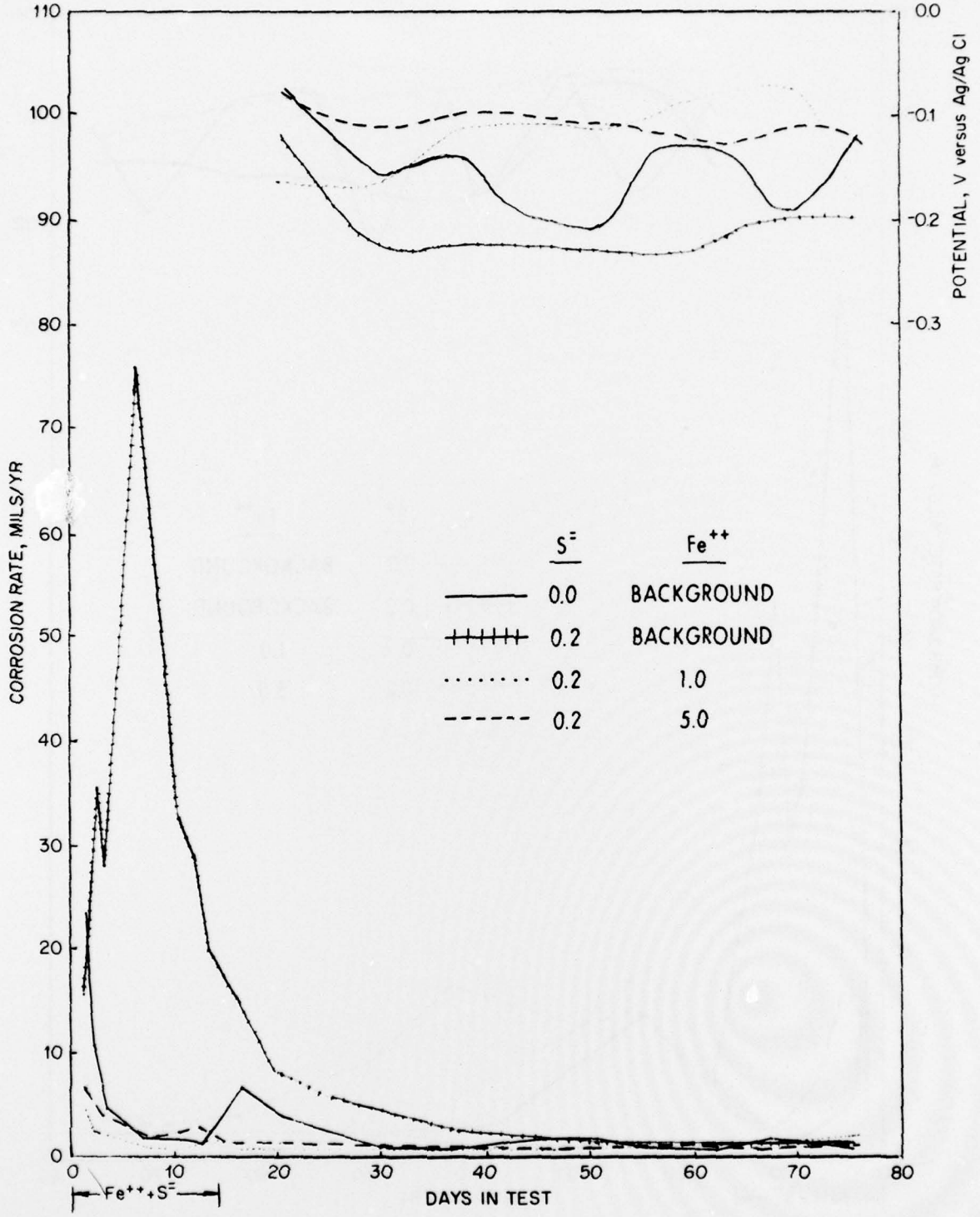

Figure 18 - Instantaneous Corrosion Rate of 70-30 Cu-Ni Electrodes in Run 4, $FeSO_4$ (Continuous, 14 days) + $S^=$ (0.2 ppm, 14 days) → Seawater

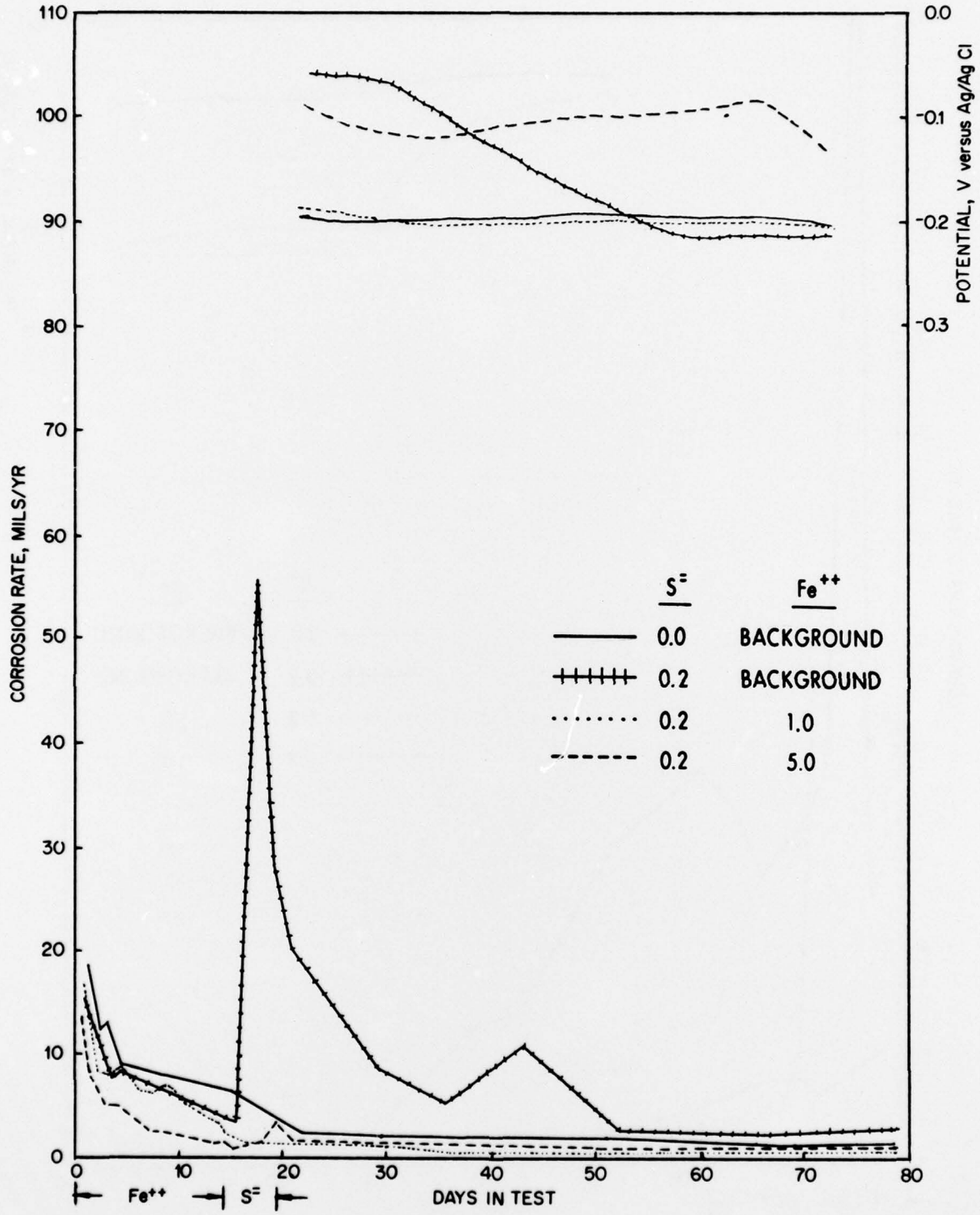

Figure 19 - Instantaneous Corrosion Rate of 90-10 Cu-Ni Electrodes in Run 1, $FeSO_4$ (2 hr/day, 14 days) → S= (0.2 ppm, 5 days) → Seawater

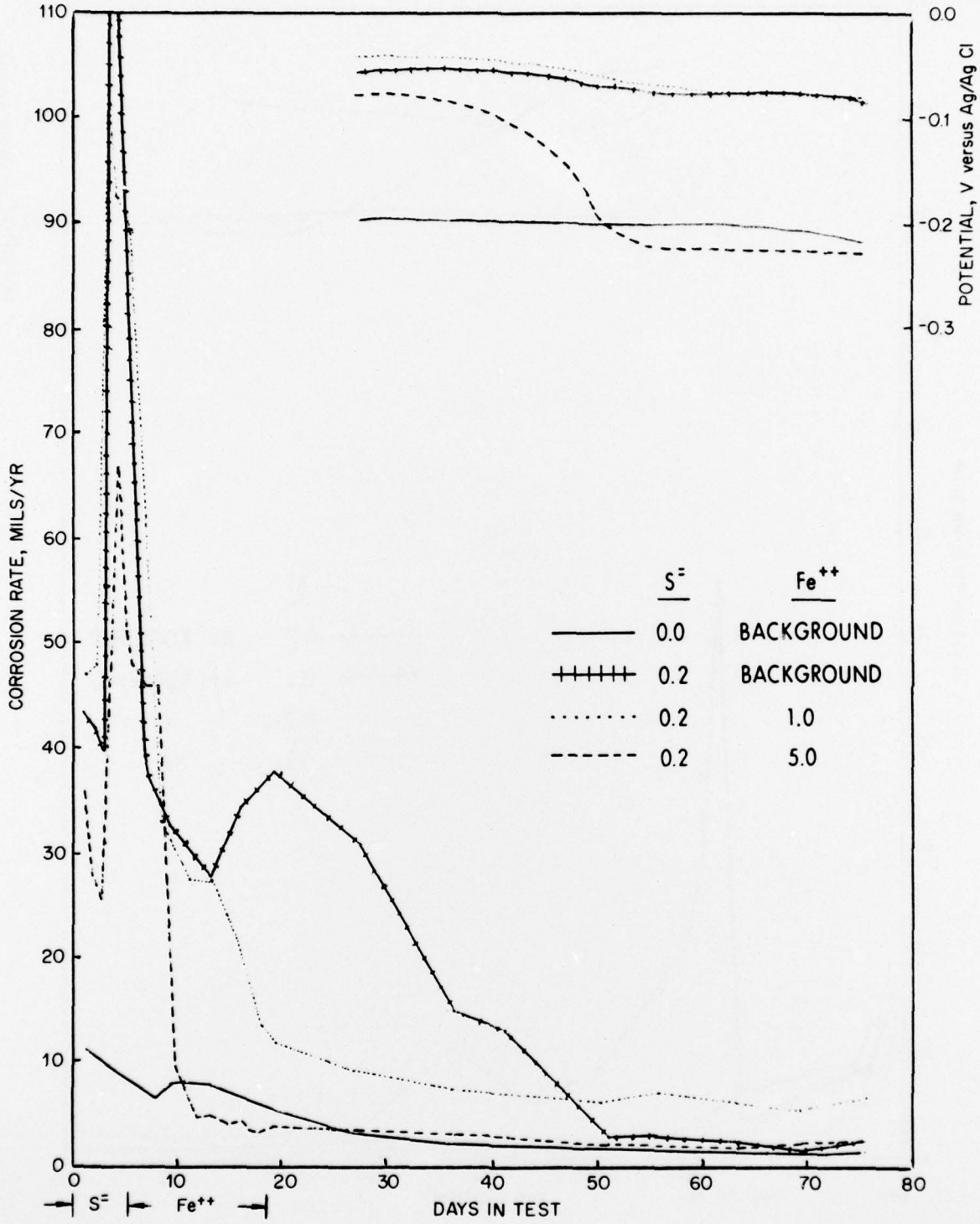

Figure 20 - Instantaneous Corrosion Rate of 90-10 Cu-Ni Electrodes in Run 2, $S^{=}$ (0.2 ppm, 5 days) → FeSO4 (2 hr/day, 14 days) → Seawater

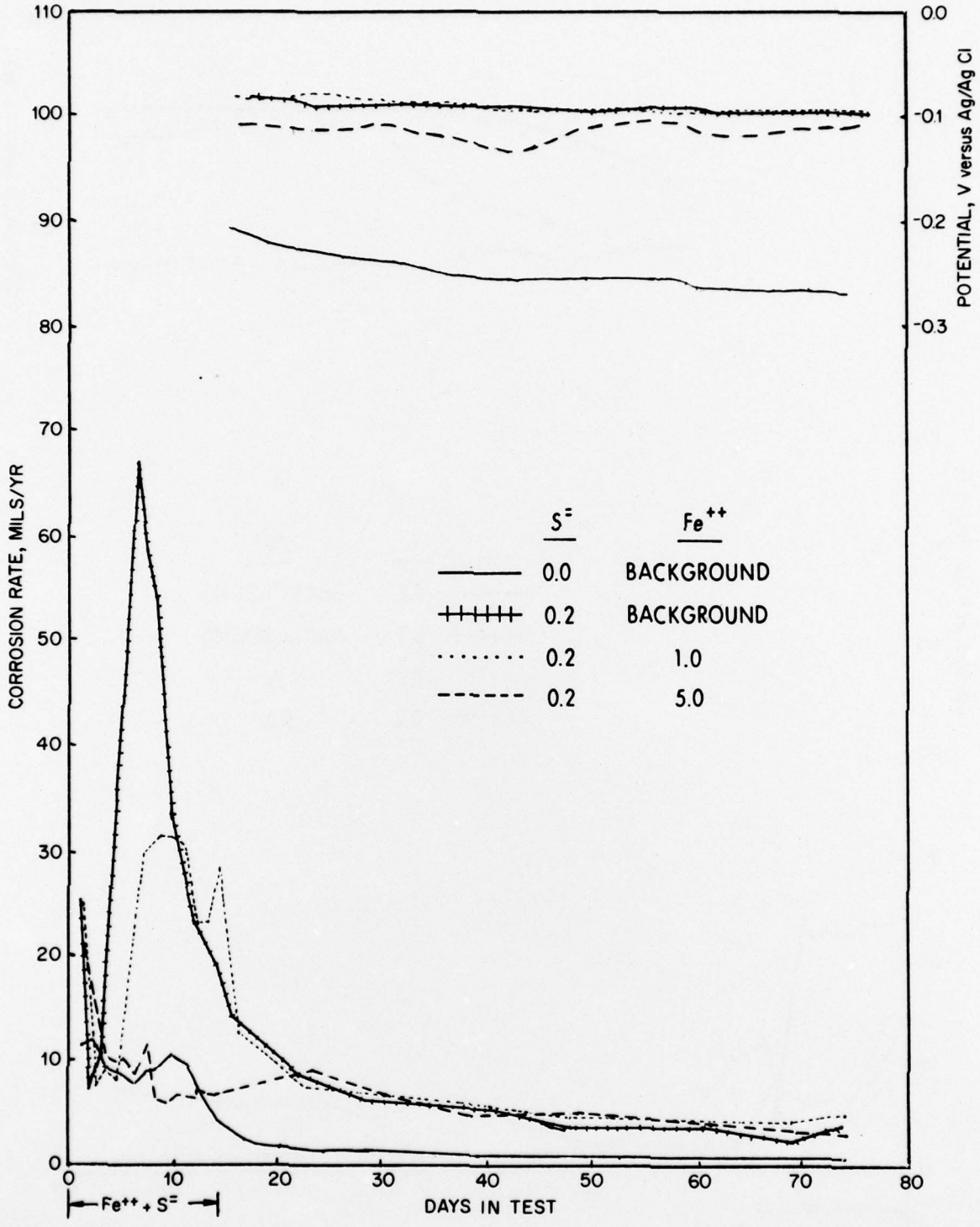

Figure 21 - Instantaneous Corrosion Rate of 90-10 Cu-Ni Electrodes in Run 3, $FeSO_4$ (2 hr/day, 14 days) + $S^=$ (0.2 ppm, 14 days)→Seawater

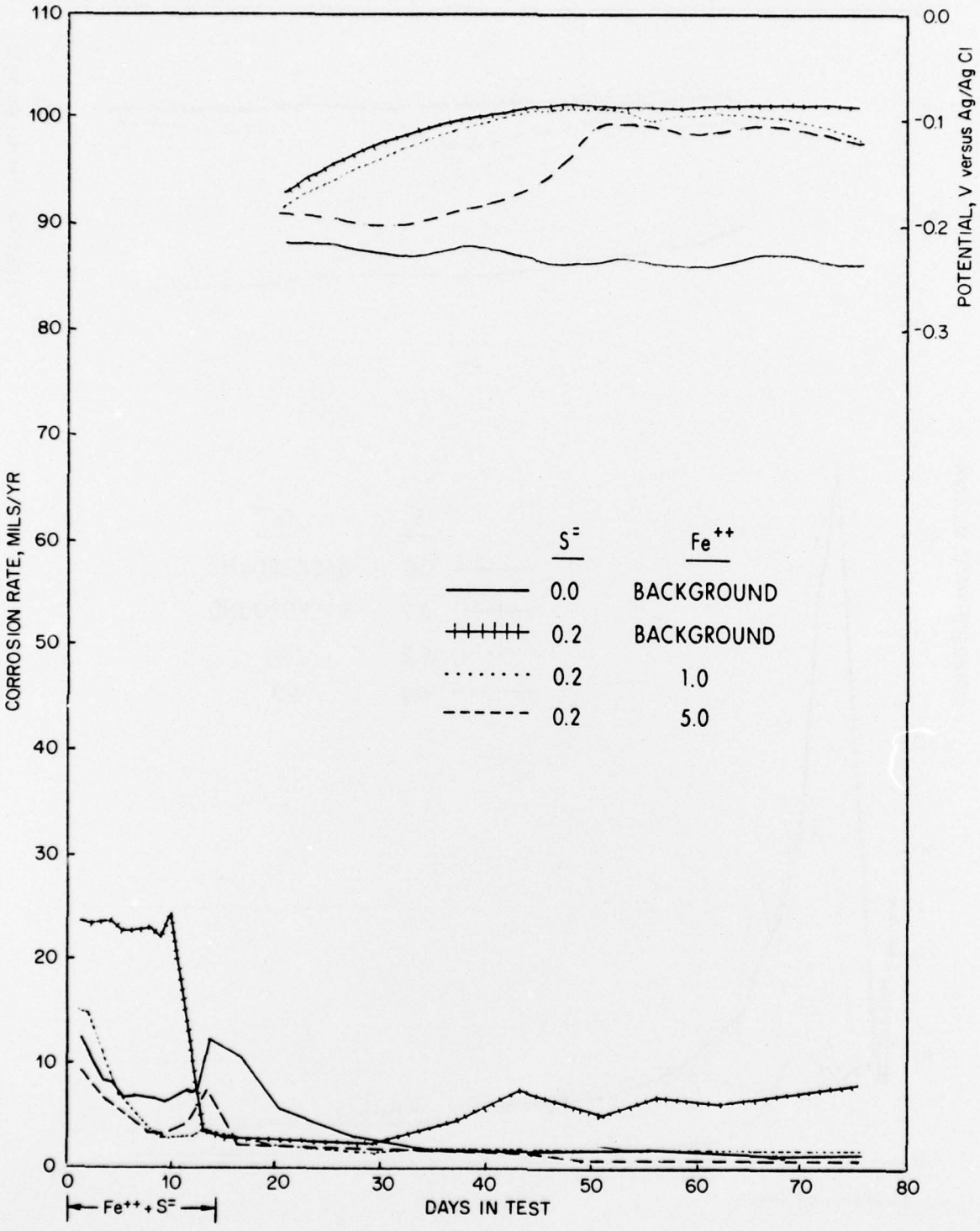

Figure 22 - Instantaneous Corrosion Rate of 90-10 Cu-Ni Electrodes in Run 4, $FeSO_4$ (Continuous, 14 days) + S= (0.2 ppm, 14 days)→Seawater

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